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Al–Pb, Mg–Pb or Mn–Pb binary cations doping in Bi-system high T_c superconductor

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Abstract

The effect of Mg–Pb, Al–Pb and Mn–Pb binary cations doping on the appearance time of high T_c 2223 phase in the Bi-system superconductor was investigated. We found that the binary cations dopants, Mg–Pb, Al–Pb or Mn–Pb tend to speed up the formation of high T_c phase distinctly and that the Al^{3+} $Mn^{3+(4+)}$ and Mg^{2+} cations occupied certain positions in the crystal lattice of the high T_c phases. They play an important role in the formation of the high T_c phases and have an effect on the structure and the superconductivity of high T_c phases.

Keywords: Bi-system superconductor; Binary cation doping; Superconductivity

1. Introduction

Since the discovery of high T_c superconductivity in Bi–Sr–Ca–Cu–O system [1], three superconducting phases of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ have been identified. They include 2201 phase ($n=1$, $T_c=20$ K), 2212 phase ($n=2$, $T_c=85$ K), and 2223 phase ($n=3$, $T_c=110$ K). However, the 2223 phase is difficult to obtain and its formation is influenced by many preparation conditions, such as composition, sintering temperature and time, atmosphere and pressure at sintering, the doped ion kind and quantity, heat-treatment method and operational procedure, etc. Numerous studies in doping have been made to synthesize high T_c 2223 phase in Bi-system superconductor and to raise the T_c [2–5].

Recently, many techniques have been developed to prepare superconductors. Doping is believed to be promising. It favors the 2223 phase formation, improves superconductivity, and may be conducive to the disclosure of the superconductivity mechanism and to the development of new superconductors. It is well known that the T_c value is significantly affected by preparation conditions, even if the superconductors have the same compositions. Similarly the effect of doping on the 2223 phase formation and its superconductivity is also influenced by the preparation conditions. Therefore, T_c value alone could not define the relationship between the doping and the formation of high T_c 2223 phase, especially as the 2201 and 2212 phases tend to coexist with the 2223 phase.

We believe that the time of high T_c phase appearance at sintering temperature might be effected by doping on Bi-system superconductor. In order to study the doping effect on the T_c and on the formation of 2223 phase in Bi-system, the high T_c phase development must be studied under specified conditions. The time of high T_c phase appearance at sintering temperature must be an important factor in the study of the doping effect on Bi-system.

To optimize the doping effect and to speed up the formation of high T_c 2223 phase in Bi–Sr–Ca–Cu–O system we carried out a series of doping experiments with binary cation dopants. In order to develop new superconductors with higher T_c and also to clarify the mechanism of superconductivity, it is necessary to investigate the relationship between doping and formation of high T_c phase, doping and structure, the structure and superconductivity of existent superconductors. In the present paper, the effect of some dopants, Mg–Pb, Al–Pb and Mn–Pb, on the formation, structure and superconductivity of high T_c phase in Bi-system was studied.

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2. Experimental section

The samples were prepared by solid-state reactions. The Bi, Pb, Sr, Ca, Cu, and M (M=Mn, Mg or Al) nitrates of A.R. grade were used for the preparation. The starting chemicals were mixed in molar ratio of Bi:Pb:Sr:Ca:Cu:M=2:0:2:1:2:0, designated as '202120', so as '202230', '(1.7) (0.3) 2230', and '(1.7) (0.2) 22 (2.91) (0.09)', respectively. These mixtures were dissolved in aqueous nitric acid solution and evaporated to dryness. After heating for 4 h at 700 °C, they were ground and pressed into round disks.

The samples, with different sintering duration at 850 °C, were characterized at room temperature with XRD (Japan Rigaku Rotaflax D/max. C), SEM (Hitachi S-520) and EDAX (Philips PV9100). The curves of electric resistance versus temperature were determined by standard four-electrode method, in which the resistance at low temperature was measured in liquid nitrogen temperature.

3. Results and discussion

3.1. Reference experiments

For comparison, firstly we carried out experiments with only-Pb-doping. For the undoped samples, the '202120' and '202230' were used as the basic compositions. After sintering for 12 h at 850 °C, the superconductive 2212 phase did not appear in the '202120' but in the '202230'. As shown in XRD, the characteristic diffraction peak (002) of the superconducting 2212 phase in the latter appeared with an intensity of $I=82$ and $I/I_0=5$. It can be seen that the starting compositions have affected the formation of superconductive 2212 phase. For only-Pb-doping, Pb is added into the above-mentioned '202230' to make '(1.7) (0.3) 2230', which took only 4 h sintering at 850 °C for the superconductive 2212 phase to appear. The intensity of characteristic diffraction peak (002) is about $I=110$ and $I/I_0=20$. It indicates that even in only-Pb-doping, the shortening of sintering time to form superconductive 2212 phase is obvious. The 2223 phase appeared in the only-Pb-doped '(1.7) (0.3) 2230' in only 76 h, but not in the undoped '202230' after 144 h at 850 °C. It suggests that only-Pb-doping promoted the formation of not only 2212 phase but also 2223 phase.

3.2. Binary cations doping

For the binary cations doping, they were designated as Mn–Pb '(1.7) (0.3) 22 (2.91) (0.09)', Al–Pb '(1.7) (0.3) 22 (2.91) (0.09)' and Mg–Pb '(1.7) (0.3) 223 (0.2)', respectively. From the XRD data in Table 1 and Fig. 1, we can see that the 2223 phase has appeared in all the three samples, but not in the only-Pb-doping sample after sintering for 6 h at 850 °C. The characteristic peak (002) of the 2223 phase is visible in Table 1, and eight, or more, peaks attributed to the 2223 phase are present in the three samples in Fig. 1 (Table 1). It is obvious that the binary cation doping can speed up the formation of high T_c 2223 phase. In contrast to the previous experimental results of only-Pb-doping, the time has been shortened from 76 to 6 h.

Table 1
The XRD data of 2223 phase at the appearing time of 2223 phase in the sample doped with Mg–Pb, Al–Pb and Mn–Pb, sintered for 6 h at 850 °C

Dopant	*hkl*	*I*	I/I_0	*d*
Mg–Pb	002	9	1	18.468
Al–Pb	002	12	1	18.448
Mn–Pb	002	8	1	18.446

3.3. Doping behaviour

Concerning Pb-doping behaviour, numerous works were reported [6,7]. Some researchers hold that Pb^{2+} is a substitute for Bi^{3+}. Others believed that it partially substitutes for Bi^{2+}, Sr^{2+} and Ca^{2+} in high T_c superconductive phase of Bi-system. The only-Pb-doping behaviour has been discussed in our previous paper [8].

For binary cations doping, Mn–Pb, Al–Pb Mg–Pb, there is little systematical research in the literature. We will report here three experimental findings in comparison with other works. Samples used in this experiment were all sintered at 850 °C and for 4, 6, 12, 28, 52, 72, 144, and 360 h, respectively. First of all, the result of XRD shows

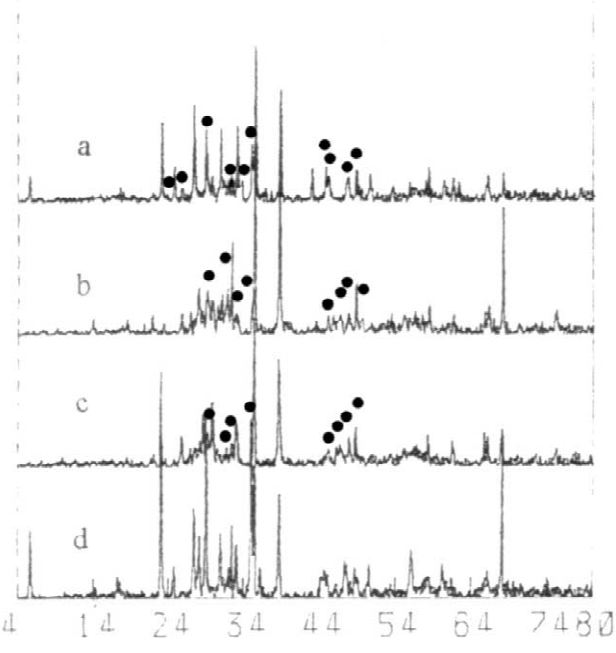

Fig. 1. XRD patterns of 2223 phase doped with Pb, Mg–Pb, Al–Pb, or Mn–Pb, respectively. '(1.7) (0.3) 22(2.91) (0.09)' for M=Mn or Al, and '(1.7) (0.3) 223 (0.2)' for M=Mg. The samples were sintered at 850 °C, for 6 h, where (a), M=Mg; (b), M=Al; (c), M=Mn; (d), doping Pb only; (●) 2223 phase.

that for the same cations doping in the specified ratio the crystal lattice parameter of high T_c 2223 phase possesses the same value with different sintering duration. The (0 0 12) crystal interplanar spacing was taken as an example of the crystal lattice parameter for its accuracy. The value of (0 0 12) crystal interplanar spacing is 0.3082(2) nm for only-Pb-doping and the same value 0.3074(2) nm for both Al–Pb and Mn–Pb, and 0.3078(2) nm for Mg–Pb in high T_c 2223 phase crystal. In this case, the changes of the crystal interplanar spacing along *c*-axis are dependent on the nature and ratio of the doping cations in Bi-system. The fact that the values of crystal interplanar spacing along *c*-axis have decreased after doping binary cations indicates that each doped cation has participated in the reaction for the formation of 2223 phase during sintering and got into the crystal lattice, to form its own 2223 phase with fixed self-crystal lattice parameter along *c*-axis. Second, from the previous point it can be seen that the crystal interplanar spacing for binary cations doping is less than that for only-Pb-doping. This phenomenon may mean that these ions, Al^{3+}, Mn^{4+} and Mg^{2+}, with smaller radii and more or equal charges can substitute for one with larger radii and less or equal electric charges, and, as a result, can shorten the lattice parameter along *c*-axis. And third, from SEM-EDAX analysis the 2223 phase doped with binary cations, Al–Pb or Mn–Pb, can be formulated as $Bi_{1.7}Pb_{0.3}Sr_2Ca_2(Cu_{1-x}M_x)_3O_y$, where $x=0.03$ and M= Al^{3+} or $Mn^{4+(3+)}$. This confirms that Al^{3+} and $Mn^{4+(3+)}$ can partially substitute Cu^{2+} with larger ion radius and less electric charge in crystal lattice of 2223 phase. This may be the reason why the crystal interplanar spacing has been shortened. Fig. 2 is the SEM micrographs of 2223 phase for Mg–Pb and Al–Pb doping. The compositions of high T_c 2223 phase in Bi-system measured by SEM-EDAX approach the theoretical ones.

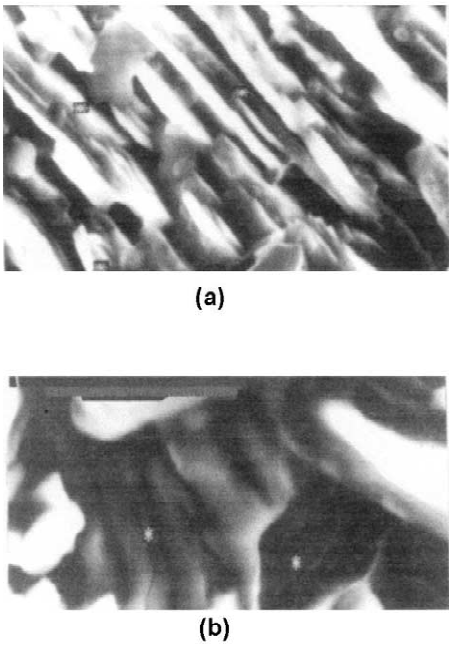

Fig. 2. The SEM micrograph, doped with Mg–Pb or Al–Pb, respectively: (a) doped Mg–Pb; (b) doped Al–Pb. (●) 2223 phase.

3.4. Ions substitution mechanism

From our experimental results we may discuss and explain which ion in the original lattice has been substituted and by which doped ion. It is not sufficient to consider only the effect of ionic radius. Other important factors have to be considered too, for example, ionic type, its outer shell electron structure, chemical property and chemical bonding type, etc. Take the much-interested Mg^{2+} as example. At the same coordination numbers, although the Mg^{2+} radius is close to Cu^{2+}, their ion types are different from each other. The Mg^{2+} outer shell electron configuration is similar to that of the inert gas atom ns^2np^6, but Cu^{2+} is close to copper ion type (Cu^+d^{10}). So, the Mg^{2+} has poor capability of substitution for Cu^{2+}. But Mg^{2+} is the same ion type as Sr^{2+} and Ca^{2+}, and all belong to the ion type that has outer electron configuration of the rare gas atom. Their outer shell electronic structure, bonding type and chemical nature are also close to each other. Moreover the difference between their ionic radii is within tolerable range of mutual substitution. Therefore, the doping Mg^{2+} might substitute for Sr^{2+} and Ca^{2+}, but not for Cu^{2+}, in despite of the fact that Mg^{2+} ionic radius is very close to that of Cu^{2+}.

For the doping Al^{3+}, it is present as spinel δ-Al_2O_3 at sintering 850 °C, based on its ionic radius and the structure of oxide phase. The δ-Al_2O_3 crystal lattice type is similar to that of the oxygen-deficient quasi-perovskite layer in high T_c 2223 phase of Bi-system. In the ABO_3 perovskite the ion B has a smaller radius. In the layer of oxygen-deficient quasi-perovskite of the 2223 phase the smaller radius ion is Cu^{2+}. The Cu^{2+} ionic radius is equal to 0.057 nm in 4-coordination and 0.065 nm in 5-coordination. The Al^{3+} ion radius in 4-coordination and in 5-coordination are equal to 0.039 and 0.048 nm [9], respectively, which is smaller than Cu^{2+} radius. The difference between their radii is within the tolerable range of substitution. Therefore, the substitution of Al^{3+} is allowed and should not result in serious distortion of the crystal lattice. So, Al^{3+} has proven to be able to occupy the position of Cu^{2+} in both 5-coordination and 4-coordination in the superconductive planes of 2223 phase, especially to increase the probability of formation of Cu–O square plane, which is responsible for the high T_c phase. These results agree with above-mentioned XRD and SEM-EDAX experiments.

For the doping Mn ions, it was verified in our previous experiment [10] that under the preparation conditions the Mn cations exist as both Mn^{3+} and Mn^{4+} in Bi-system superconductor. The radius of Mn^{4+} in 4-coordination is 0.039 nm and Mn^{3+} in 5-coordination is 0.058 nm. They may partially substitute for Cu^{2+} and occupy Cu^{2+} positions in 4-coordination and 5-coordination, respectively, in the superconductive Cu–O planes. Therefore, the two

superconductive Cu–O planes have increased in the probability of their formation, especially the Cu–O square plane which is needed by high T_c phase. So $Mn^{3+(4+)}$ ions could shorten the hours of formation of 2223 phase.

3.5. The effect of substitution

Based on the above discussion, doping with Mg^{2+}, Al^{3+} or $Mn^{3+(4+)}$ results in substitution of the smaller radius ions for the larger ones. On the other hand, the substitutions cause reduced interplanar spacing along *c*-axis direction in the doped 2223 phase of Bi-system. In the cell of 2223 phase, the layer sequence along *c*-axis in the crystal can be represented as follows: $BiO \cdot SrO \cdot CuO_2 \cdot Ca \cdot CuO_2 \cdot Ca \cdot CuO_2 \cdot SrO \cdot Bi_2O_2 \cdot SrO \cdot CuO_2 \cdot Ca \cdot CuO_2 \cdot Ca \cdot CuO_2 \cdot SrO \cdot BiO$. After sintering under atmosphere, the superconductor of Bi-system is P-type [11,12]. It is known that the superconductivity mainly originates from Cu–O planes, and from the Bi–O layers acting as carrier reservoir. Substituting Mg^{2+} for Ca^{2+} and Sr^{2+}, the reduction of the distance between Cu–O plane and Bi–O layer can strengthen their electric and structural coupling. Therefore, it can enhance superconductivity of the doped superconductor and promote stability of the crystal structure to speed up formation of high T_c phase.

Moreover, the substituting ion with a smaller radius diffuses faster than with a larger radius during thermal reaction at sintering temperature. They get into the position in crystal lattice more easily, and distribute more suitably for constructing 2223 phase and more increase in the formation probability of Cu–O planes, which are particularly needed for the formation of 2223 phase. Thus doping of these smaller radius ions, such as Mg^{2+}, Al^{3+} and $Mn^{3+(4+)}$ obviously shortens the induction period of high T_c 2223 phase, from 76 to 6 h as our experiment has indicated.

Besides this, the substitution of Al^{3+} and $Mn^{3+(4+)}$ for Cu^{2+} is that of unequal valence. The substitution of higher valence ions has brought about strengthening coulomb attraction between the cations and the anions, hence improving the stability of 2223 phase. On the basis of energy effect, the reason why the crystal stability is increased is that doping substituting ions have higher valence and larger energy coefficient. Therefore the substitution can enhance crystal lattice energy. This explains why above doping ions can speed up formation of high T_c 2223 phase.

3.6. Reduction of interplanar spacing

The structure of the crystal cell of 2223 phase for Bi-system superconductor is shown in Fig. 3 [13]. In the unit cell there are two kinds of O^{2-} coordination polyhedrons, the pyramid and the square plane, which are filled with Cu^{2+}. The pyramid polyhedron proves to be O^{2-} close-packing structure and hardly capable of shortening

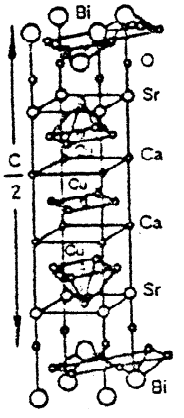

Fig. 3. The crystal lattice structure of high T_c 2223 phase.

the interplanar spacing along *c*-axis, because the height of the pyramid is always close to value of close-packing, 0.2122 nm, whether from our calculating or from other experiments [6].

On the Cu–O square plane structure layer in the unit cell, both its sides along *c*-axis have plenty of free space available for shortening. Fig. 4 is a part of quasi-perovskite layers in crystal of the 2223 phase, from Cu–O square plane to pyramid Cu–O structure layer. On both sides of the Cu^{2+} in the Cu–O square plane, upper and under, the anion layers are O^{2-} layers of the pyramid bottoms. From Fig. 4, we can see that between Cu–O square plane 'A' and pyramid bottom Cu–O plane 'C' there is structure layer 'B', Ca-layer. The distance between Cu–O square plane and pyramid bottom Cu–O plane is ~0.3223 nm in Ref. [6]. But when the sum of thickness of the three layers as close-packing structure are calculated, the distance between Cu–O square plane and pyramid bottom Cu–O plane is much less than this value ~0.3223 nm. This shows that the free space between the two Cu–O planes is great enough to shorten. As mentioned above, with doping Mn or Al ion the interplanar spacing along *c*-axis is reduced. It can be interpreted that the distance between O^{2-} layers of

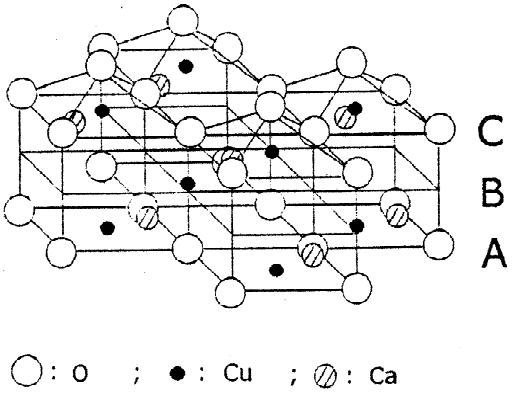

Fig. 4. Crystal structure layer from 5-coordination Cu–O plane to 4-coordination Cu–O square plane in the 2223 phase crystal.

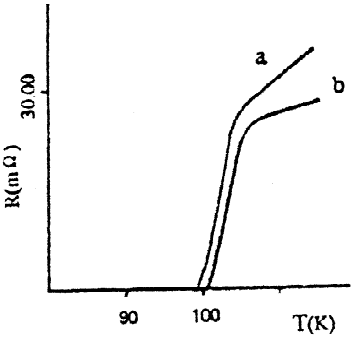

Fig. 5. The *R–T* curve, (a) doped Mg–Pb, (b) doped Al–Pb.

pyramid bottom and Cu–O square plane along *c*-axis is reduced. The reduction maybe results from the substitution of small radius ions Al^{3+} or Mn^{4+} for Cu^{2+}. The substitution of the small radius ion for Cu^{2+} can speed up the formation of 2223 phase, because the diffusion of the small ion is faster than that of the large one during solid state reaction. As mentioned above, from SEM-EDAX detection, the chemical formula of 2223 phase in doped samples is $Bi_{1.7}Pb_{0.3}Sr_2Ca_2(Cu_{1-x}M_x)_3O_y$ $x=0.03$, M= Al^{3+}, $Mn^{4+(3+)}$, which showed the substitution of small radius ions Al^{3+} or Mn^{4+} for Cu^{2+}.

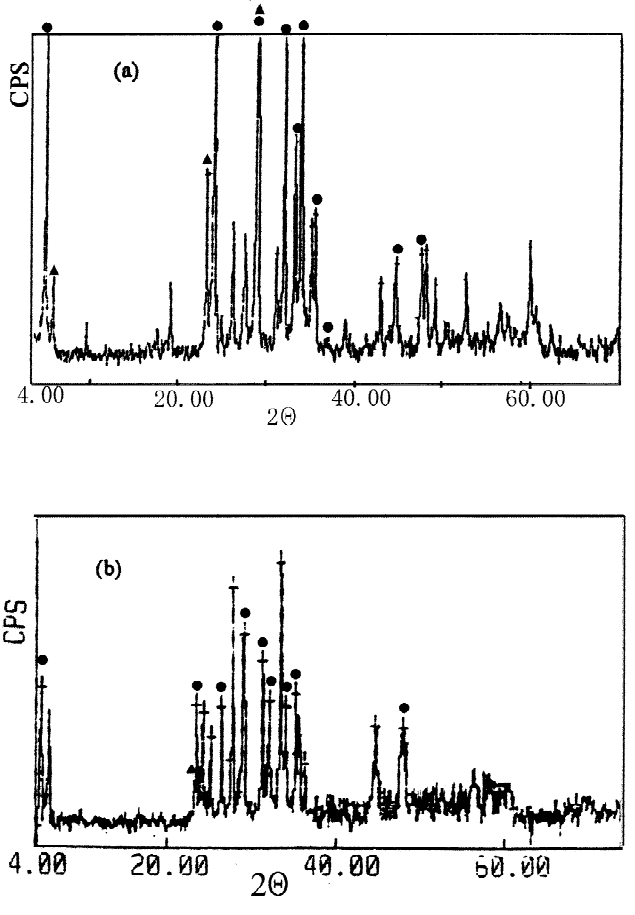

Fig. 6. The XRD pattern of 2223 phase in the sample doped with Mg–Pb (a) and Al–Pb(b), (●) 2223 phase, (▲) 2212 phase.

Table 2
The XRD data of 2223 phase in the samples doped with Mg–Pb (a) and Al–Pb (b)

Dopant	*hkl*	*I*	I/I_0	Duration
Mg–Pb	002	1004	53	280 h
Al–Pb	002	278	56	144 h

Fig. 5 shows *R–T* curves of the samples with the high T_c 2223 phase as the predominant phase are experimentally determined. Fig. 5a represents the curve of the sample doped Mg–Pb and Fig. 5b the doped Al–Pb. The XRD results are shown in Fig. 6 and Table 2. Fig. 6a is the XRD pattern of Mg–Pb-doping samples sintered for 280 h, at 850 °C. In the sample, high T_c 2223 phase is over 90%. Fig. 6b is the pattern of Al–Pb-doping sample sintered for 144 h at 850 °C, in which the high T_c 2223 phase is predominant.

4. Conclusions

Doping with ions of Al^{3+}, $Mn^{4+(3+)}$ or Mg^{2+} significantly shorten the sintering duration for the formation of high T_c 2223 phase (Fig. 6). The sintering hours at which the high T_c 2223 phase starts to appear is an important criterion for the assessment of the effect of doping. The doping ions, Al^{3+}, Mn^{4+} or Mg^{2+}, participate in the sintering reaction and get into the crystal lattice and substitute for Cu^{2+}, Ca^{2+} or Sr^{2+}. The substitutions of the doping ions not only depend upon the ionic radius but also upon the cation type, its outer shell electron structure and the bonding property. The binary doping improves the superconductivity in comparison with the only-Pb-doping.

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